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Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: tracing sediment and organic matter

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Organic matter, cycled through intensive grasslands, presents a poorly understood but important source of colloids and sediment that may significantly contribute to undermining downstream water quality (Haygarth *et al.*, 2006). In this respect, tracers provide a range of new opportunities that may help contribute to new or improved understandings. Tracers can be natural or anthropogenic compounds, which are either already present in the environment or are experimentally introduced. The very presence or absence of the tracer at the point of measurement can give qualitative information on whether and when an individual source is contributing. If basic key assumptions such as homogeneous incorporation of the tracer into transported soil/sediment, conservative behaviour of the tracer and non-preferential transport of the tracer are not violated, then more quantitative information can be derived with mixing models or detailed mass balance calculations. Well-established sediment-tracing techniques include sediment mineralogy (Wall and Wilding, 1976), mineral magnetics (Dearing, 2000) and environmental radionuclides (Walling, 2005). These and other commonly used tracing properties are illustrated and discussed further in Foster and Lees (2000) (Figure 1).

The most commonly used and established approach is the sediment fingerprinting method, which identifies a range of measurable characteristics associated with a particular sediment source and then uses modelling techniques to apportion a given sediment mixture between those different sources. Source types that have been identified in this way are surface and subsurface soil, topsoil from areas of different land use, channel banks, different soil or geological zones, different tributaries and urban sources such as road dust and solids from sewage treatment works (e.g. Carter *et al.*, 2003; Gruszowski *et al.*, 2003; Owens *et al.*, 2000; Russell *et al.*, 2001; Walling and Woodward, 1995). The relative enrichment or depletion of fallout environmental radionuclides (such as ^{137}Cs, ^{7}Be and unsupported ^{210}Pb) has also been used to provide information on sediment redistribution either through erosion processes (Blake *et al.*, 1999; Walling and He, 1999), through agricultural and land management practices (e.g. tillage erosion in arable cultivation (Quine, 1999), or in harvesting of forests (Wallbrink *et al.*, 2002)). This spatially distributed information is highly important for understanding soil erosion processes.

However, one of the main drawbacks of these approaches is the uncertainty in the amounts of tracer input, both spatially and in terms of preferential attachment to different particle sizes. An alternative approach, that presents some ideal opportunities for studying intensive grassland catchments, is through manipulation experiments, where the quantity and characteristics of the added tracer are tightly controlled. Exotic particles such as fluorescent (Bricelj and Misic, 1997; Marsh *et al.*, 1991; Young and Holt, 1968) and magnetic (Ventura *et al.*, 2001) beads have been used in the past. More recent work has focused on the potential for using rare earth oxides (Polyakov and Nearing, 2004;

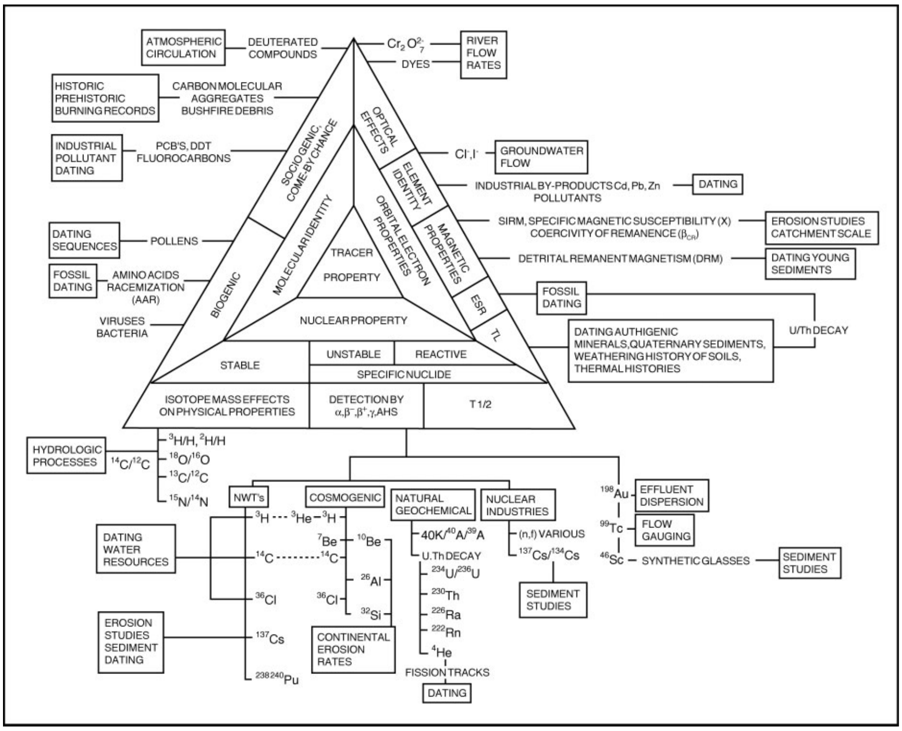

Figure 1. Fundamental properties of earth materials, which might be used for dating and tracing sediment sources (from Foster and Lees, 2000, reproduced by permission of John Wiley & Sons, Ltd.)

Zhang *et al.*, 2001) and DNA fragments (Mahler *et al.*, 1998). Ideally, tracers used in manipulation experiments should have similar behaviour to the particles that they are intended to mimic, have great sensitivity and be available as multiple tracers.

It has long been assumed that an increase in pollutants observed in the water courses of intensively managed grassland areas were a result of recent farming activities on the land, such as the application of managed manures or fertilizers. However, this link has never been physically demonstrated and this is one of the potentially exciting contributions that manipulative tracing approaches may offer. Thus, in examining sediment and colloid transfers from intensive grasslands, particularly in relation to potential contaminants such as phosphorus, there is a fundamental need to:

1. apportion sources of sediment and colloids and associated pollutants between soil processes and agricultural amendments; and
2. understand the timing and response of the different transfer pathways (dissolved, colloidal and particulate) by which agricultural amendments (manure, fertilizer) contribute to the quality of receiving waters.

Tracing agricultural diffuse pollutants is difficult. Established sediment-tracing techniques, such as those outlined above, have in the past been used to identify the source of sediment at a broad catchment scale, and by implication, the attached phosphorus mobilized by erosion processes. However, they have neither addressed the question of the role of agricultural amendments nor really established a direct link with phosphorus. The difficulty with tracing the sediment carrier rather than phosphorus itself is that the phosphorus mobilized by dissolution processes, which is thought to be the majority of phosphorus transferred from grazing systems (Nash and Halliwell, 1999), attaches to sediment during transport. Consequently, the source of the phosphorus carrier need not necessarily reflect the phosphorus source and no techniques are available for directly tracing phosphorus mobilized by dissolution processes (except perhaps the use of radio-isotopes ^{33}P and ^{32}P, which is only feasible within contained laboratory experiments).

A key opportunity and need within intensive grasslands is to focus on tracing the fate of applied manures; in the United Kingdom approximately 90 million tonnes of solid manure and slurry are annually applied to agricultural land, and grazing livestock also return dung and urine to the soil. Slurry applied to intensive grasslands therefore presents a significant source of phosphorus, sediment and colloids that may easily be transported in surface and subsurface drain flow. Bellamy *et al.* (2005) noted that the relative rate of loss of carbon from UK soils increased with soil carbon content, irrespective of land use. The organic matter content of (intensive) grasslands is generally higher than land under arable cropping pointing to a potentially higher loss of carbon (and phosphorus associated with carbon) from grassland compared to arable systems.

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Three complementary techniques are suggested to attempt to elucidate the role of agricultural amendments in relation to both sediment/colloids and associated phosphorus: natural abundance of carbon isotopes, natural fluorescence and particulate tracers.

The natural abundance ^{13}C tracer technique is potentially very useful as a tracer of organic matter sources in fluvial sediment systems (McConnachie and Petticrew, 2006). Because various forms of phosphorus play a role in soils and some of those (organic) forms are, critically, linked with carbon (Bol *et al.*, 2006), it should follow that by tracing slurry-derived carbon it would also be possible to trace slurry-derived organic phosphorus, assuming the carbon-phosphorus link remains largely intact, at least over the short term. This approach is possible using a natural abundance ^{13}C carbon labelling technique (Bol *et al.*, 2000). Most of the natural carbon-isotope fractionation occurs during photosynthesis (Farquhar *et al.*, 1989). The photosynthetic pathway of C_3 plants discriminates against $^{13}CO_2$, whereas within C_4 plants the discrimination does not take place. The result of this metabolic variation is that C_3 plants have a relatively low $\delta^{13}C$ (typically -32 to -20‰) while C_4 plants have a relatively high $\delta^{13}C$ (typically -17 to -9‰) (Boutton, 1991). By feeding cattle with maize (a C_4 plant) silage rather than the usual ryegrass (a C_3 plant) silage, the carbon in slurry derived from maize-fed cattle will, naturally, become more enriched with ^{13}C. By looking for such an enriched ^{13}C signature in the carbon in drainage waters from an intensive grassland applied with maize-based slurry compared with a grass-based slurry, it should be possible to discern the proportion and type of material that is directly derived from the slurry and that which has come from the 'native' soil. This assumes that the soil processes that affect maize and grass slurries are the same. Indeed, a recent field experiment has indicated that slurry-derived organic C (and hence potentially organic phosphorus) lost from intensive grasslands can vary from 10–75% (maxima occurring shortly after application and during storm events). Furthermore, the slurry-derived carbon in the drainage waters remained detectable with this technique for up to 2·5 months after the slurry had (visually) disappeared from the surface (Preedy *et al.* in preparation). Measurements of the isotopic ratios of both dissolved (operationally defined as $<0{\cdot}45$ μm) and particulate forms could then be used to differentiate dissolved and particulate pathways (Amelung *et al.*, 1999; Bol *et al.*, 1999).

The presence of animal wastes and manures in water can also be indicated by natural fluorescence characteristics. Recent advances in fluorescence spectroscopy allow rapid determination of excitation-emission matrices, which enable the identification of different fluorophores within the sample (Baker, 2002b; Stedmon *et al.*, 2003). Typically, in natural waters, five fluorescence peaks may be identified and ascribed to different types of material, notably protein groupings, predominantly tyrosine-like and tryptophan-like substances, and the high molecular weight organic molecules described as fulvic-like and humic-like substances. Baker (2002a) also analysed a number of different farm wastes in terms of their fluorescence properties and results suggested that these could leave a distinct signature in river waters because of their high protein-like fluorescence intensity. Spatial variation in dissolved organic matter sources at the catchment scale (Baker and Spencer, 2004) and correlations between tryptophan-like fluorescence and phosphorus have subsequently been explored (Baker and Inverarity, 2004). Fluorescence techniques have also been applied to the identification of runoff pathways and the contribution of peat-decomposition products in upland catchments (Newson *et al.*, 2001) but, as yet, the techniques have not been applied to understanding the temporal dynamics and pathways through which animal wastes enter headwater streams. While natural fluorescence is currently only used as an indicator, there is potential to develop the method to quantify the amounts, sources, timing and pathways of animal waste delivered to receiving waters. Although this step is not straightforward, fluorescence has the advantage of natural occurrence, high sensitivity and rapid inexpensive measurement.

Slurry is composed of organic material from dung, bedding, foodstuffs, urine and often other farm 'washings' that present various opportunities for particulate tracers. Typically, slurries have a dry matter content of about 6% (Chadwick and Chen, 2002), and as such particulate and colloidal pathways are important in the transport of potential contaminants. The carbon-isotope tracing technique as applied to the particulate fraction will provide information on the response of these pathways. However, the comparison of fields amended with either C_3 or C_4 slurries using the natural abundance tracer ^{13}C technique is not optimal in fields where C_4 crops (e.g. maize) have grown. Carbon isotopes also only provide a single tracer approach, whereas the use of exotic materials has the potential to provide multiple tracers. Both particles coated with fluorescent dye and DNA-labelled particles have the potential to provide multiple tracers and satisfy the requirement for high sensitivity. The main problem with exotic particles is the extent to which they will mimic the behaviour of the slurry particulates. Particle size, density and shape characteristics can be matched to replicate the hydraulic behaviour of the slurry. However, such measurements have not routinely been done on this type of inherently varied material. For example, initial measurements suggest that the <2 mm fraction of dairy slurry has a particle size distribution with a clear peak at 150–200 μm. Additionally, the cumulative percentage particle size line also indicates a shoulder at 27–37 μm which points to an additional peak in the <45 μm fraction (Figure 2). Furthermore, initial measurements of the

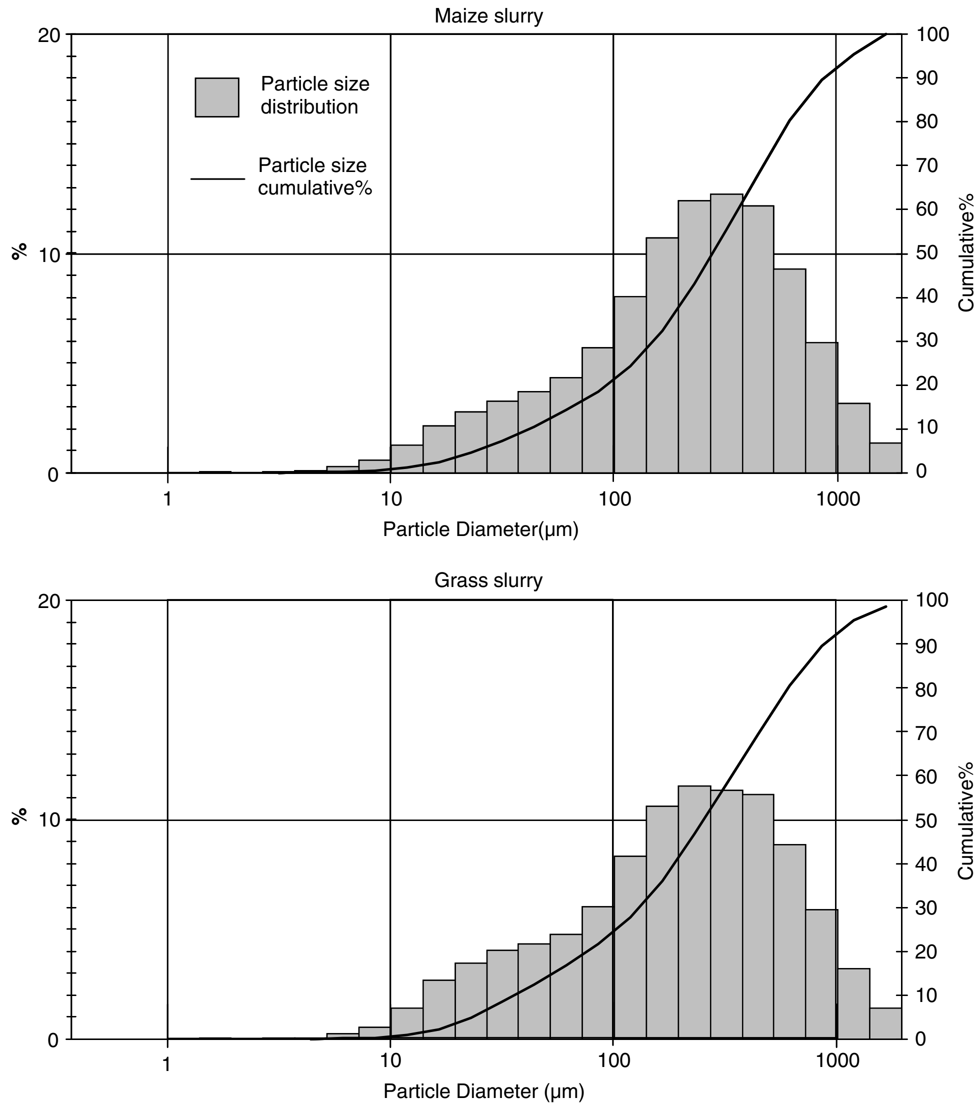

Figure 2. Size distribution of the <2 mm particle fraction in dairy slurries from maize and grass-based farm systems determined using a Malvern Laser Sizer

<45 μm particle fraction indicate an average density of 1·67 g cm^{-3} suggesting that the slurry includes both organic and mineral material components. On examination, particles within the 20–40 μm size range show highly varied shapes as shown in Table I. While these properties may be more or less replicated in an artificial tracer, there is less potential to mimic the electrical and chemical characteristics of slurry particles and so the comparison with the carbon-isotope measurements is very important—it will either provide corroboration of measurements from different techniques or provide information on the importance of other processes not mimicked by the artificial tracers.

To summarize, we believe that one of the future challenges in understanding the transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands is to quantify the contribution of organic matter losses. In particular, we see a fundamental need to:

Table I. Qualitative assessment of the shape of 225 particles in the 20–40 μm particle size range of maize slurry determined optically through a ×400 microscope

Description of shape	Percentage of particles
Long thin strap-like particles (length : width ratios >2; generally ≫2)—some with smooth sides; some intricate	19
Triangular/diamond shapes with sharp corners	7
Roundish aggregates with intricate edges	17
Round or oval shapes with smooth edges (a few were completely spherical but others had length : width ratios of 2)	29
Rectangular shapes generally smooth edges with subrounded corners (length : width ratios range from about 1 to 2)	28

- apportion sources of sediment and colloids and associated pollutants between soil processes and agricultural amendments; and

Table II. Summary of potential of the discussed novel tracer techniques to elucidate slurry, sediment and colloid losses from intensive grasslands

Technique	State of art	Pathway	Advantages	Disadvantages
Stable carbon-isotope (^{13}C)	Naturally labelled (C_4) slurry not applied at catchment scale	Dissolved and particulate phase	No rapid degradation applicable to both dissolved and solid phase	Need for both C_4 and C_3 slurries, i.e. need to feed animals on pure C_4 and C_3 diets
Natural fluorescence	Used in stream monitoring at catchment scale and on samples of animal waste; not used to look at slurry transfer processes at plot scale	Dissolved phase	Natural occurrence Highly sensitive High speed and low cost of analysis	Indicator only Need to factor out fluorescence decay/change with time Correction for background fluorescence
Artificial fluorescence	Not usually applied to land-based processes	Particles	Highly sensitive Relatively long-lived Specific, i.e. use of different labels for different sources/pathways/characteristics	Cost of analysis Relatively limited number of labels How well is behaviour of slurry, sediment or colloids in land-based processes replicated?
DNA labels	Under development	Colloids	Highly sensitive Long-lived Potential for very large number of labels	Limited size range available at present; unproven

- provide quantitative information on the contributions, pathways and dynamics of organic sources of sediment and colloids that may help inform new models (Krueger *et al.*, 2007).

To this end, we have identified a number of novel tracing techniques applicable at both the plot and small catchment scale. The potential of these techniques, together with their advantages and disadvantages, are summarized in Table II. The techniques are complementary in terms of the different components and pathways which they are designed to trace. Use of the techniques in tandem allows for a certain amount of cross-checking and corroboration in the interpretation of experimental results. By this means, confidence in the techniques will be established, enabling them to be used more widely and, thus, providing the capability for understanding the role of agricultural amendments in the transfer of sediment and colloids from intensively farmed grassland systems.

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